

PYROELECTRIC LIQUID CRYSTAL MATERIALS FOR UNCOOLED IR SENSORS

JULY 1999

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ABSTRACT

We have developed new ferroelectric liquid crystalline materials with large pyroelectric coefficients (p). Data on p have been obtained using the Byer-Roundy technique that allows a direct determination of p by ramping the temperature of the sample at a fixed rate. Our results show that the liquid crystalline materials developed by us exhibit p values in the range of 30-150 nC/cm²K without any applied bias voltage, while p values of 150-300 nC/cm²K have been observed in the presence of bias voltages. We also discuss the figure of merit of these materials for uncooled IR sensing applications.

1.0 INTRODUCTION

Smectic liquid crystals are characterized by layered arrangement of molecules. The molecules are normal to the layer in the smectic-A phase while they are tilted in the smectic-C* phase. The tilted smectic C* (Sm-C*) phase is ferroelectric with a spontaneous polarization while the smectic-A phase has no polarization and hence equivalent to the paraelectric phase in solid ferroelectrics.

Polarization (P) in the Sm-C* phase varies with temperature and goes to zero at the Sm C*-Sm-A transition obeying the Curie behavior¹. The pyroelectric coefficient (p), defined as dP/dt , therefore shows a divergence close to the phase transition. Although this effect has been known in liquid crystals for a long time², the value of p observed so far has been too low to be of importance for applications. Specifically, for uncooled IR sensing applications, perhaps the most important material requirement is a large value of the pyroelectric coefficient³.

In this paper we will report the results of our studies on a newly developed family of liquid crystals based on a siloxane unit in the chemical structure of the molecules. We show that these materials exhibit very high values of p and are suitable for applications.

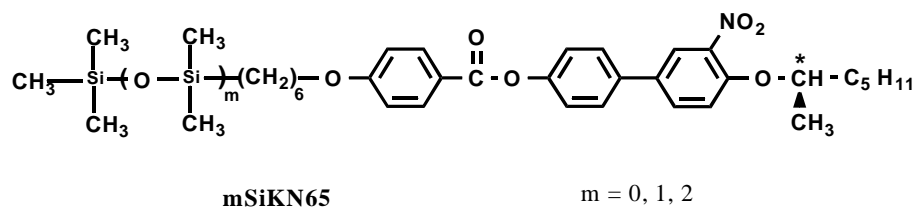
Form SF298 Citation Data

Report Date <i>("DD MON YYYY")</i> 00071999	Report Type N/A	Dates Covered (from... to) <i>("DD MON YYYY")</i>
Title and Subtitle Pyroelectric Liquid Crystal Materials for Uncooled IR Sensors		Contract or Grant Number
		Program Element Number
Authors		Project Number
		Task Number
		Work Unit Number
Performing Organization Name(s) and Address(es) Center for Bio/Molecular Science and Engineering Code 6900, Naval Research Laboratory Washington, DC 20375		Performing Organization Number(s)
Sponsoring/Monitoring Agency Name(s) and Address(es)		Monitoring Agency Acronym
		Monitoring Agency Report Number(s)
Distribution/Availability Statement Approved for public release, distribution unlimited		
Supplementary Notes		
Abstract		
Subject Terms		
Document Classification unclassified		Classification of SF298 unclassified
Classification of Abstract unclassified		Limitation of Abstract unlimited
Number of Pages 7		

2.0 EXPERIMENTAL

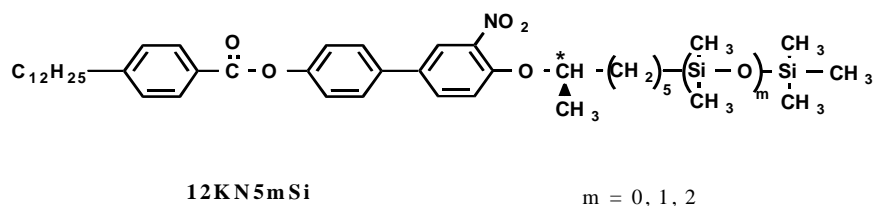
Materials: The liquid crystals developed by us belong to two classes of materials⁴. In one of them (Fig. 1) the feature of the chemical structure is the siloxane (or SiO) unit that is at one end of the molecule. In the second class of materials (Fig. 2), the siloxane unit is located near the chiral center (marked *).

The chemical structures of the materials studied as well as their phase transition temperatures are given in Figures 1 & 2.



Material	Phase Sequence (°C)
SiKN65	K < -20 SmC* 48.2 SmA 51 Iso
DSiKN65	K < -20 SmC* 40.5 SmA 55 Iso
TSiKN65	K < -20 SmC* 28 SmA 57 Iso

Figure 1: Chemical structure and transition temperature of mSiKN65 materials



Material	Phase Sequence (°C)
12KN5Si	K < -20 SmC* 47 SmA 61 Iso
12KN5DSi	K < -20 SmC* 41.5 SmA 59 Iso
12KN5TSi	K < -20 SmX 46 SmA 56 Iso

Figure 2: Chemical structure and transition temperature of 12 KN5mSi materials

Pyroelectric Measurements:

To determine the pyroelectric coefficient directly, the Byer-Roundy³ method is used. In this measurement, the temperature is increased linearly and both the temperature and pyroelectric current are measured as a function of time. A Micromanipulator H/C 1000 thermal chuck system, controller and DC power supply, provided the temperature control. The system was configured to minimize electrical noise in a Light-Tight enclosure (also from Micromanipulator.) A Keithley 6517A Electrometer/High Resistance Meter is used to measure the resistance and the built-in voltage source provided the bias voltage for some of the measurements. A Keithley 2002 Multimeter is used to measure the resistance of a thermistor from which the temperature of the sample is obtained. A workstation equipped with a National Instruments GPIB interface and LabviewTM 5.1 allowed for computerized data acquisition.

To calculate the pyroelectric coefficient, p , the following equation is used:

$$p = i/A \cdot \Delta T/\Delta t,$$

where i is the current, A is the area of the sample, and $\Delta T/\Delta t$ is the discrete time derivative of the temperature.

The sample configuration consists of a liquid crystal film of thickness 3.6 μ m confined between two glass slides, one coated with Indium-Tin-Oxide (ITO) and the other with gold. Both plates act as electrodes and a SiO_x alignment layer obliquely deposited over the ITO promotes liquid crystal alignment. Prior to the measurements of the pyroelectric coefficients, the liquid crystal was heated to the isotropic phase and then cooled to the smectic A phase under the presence of an applied electric field to obtain a “domain free” sample. This ensured that the liquid crystal molecules are preferentially oriented resulting in a large area of well-aligned sample. Once the alignment is achieved in the liquid crystalline phase, the electric field is removed. It was expected that the liquid crystal should now retain most of its dipole order and hence the material should exhibit a pronounced value of p at zero bias voltage conditions. Results in the next section show that this is indeed the case.

3.0 Results and Discussion

In Figure 3, a typical data run shows current and temperature dependence in time. Three temperature ramps, both up and down in temperature are performed on each of three samples and only data in the temperature range of interest is shown. The temperature ramp rate during the run varies from 0.8 C/min to 1.6 C/min. However, the calculation of p is performed over a time interval of about 0.5 sec, small enough to assure linearity in temperature. From the current data, a MatlabTM routine is used to calculate p as a function of temperature.

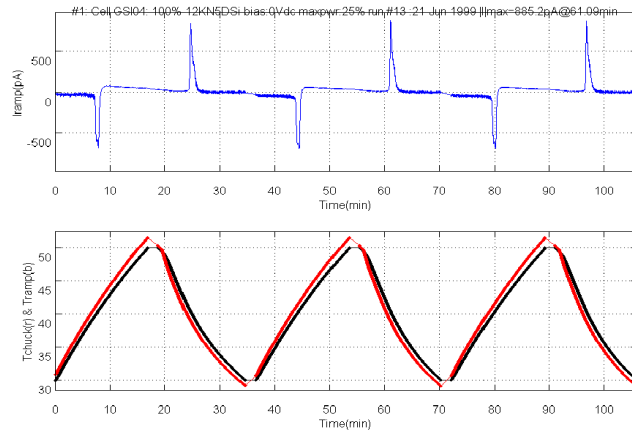


Figure 3. Byer-Roundy current measurement for 12KN5DSi material. Cell thickness $3.3 \mu\text{m}$, 0.36cm^2 area and 0V DC Bias.

Figures 4 a, b and c show the pyroelectric data for three materials: DSiKN65, TSiKN65 and 12KN5DSi. To our understanding, *these data are the first direct measurements of p for liquid crystals recorded in the literature.*

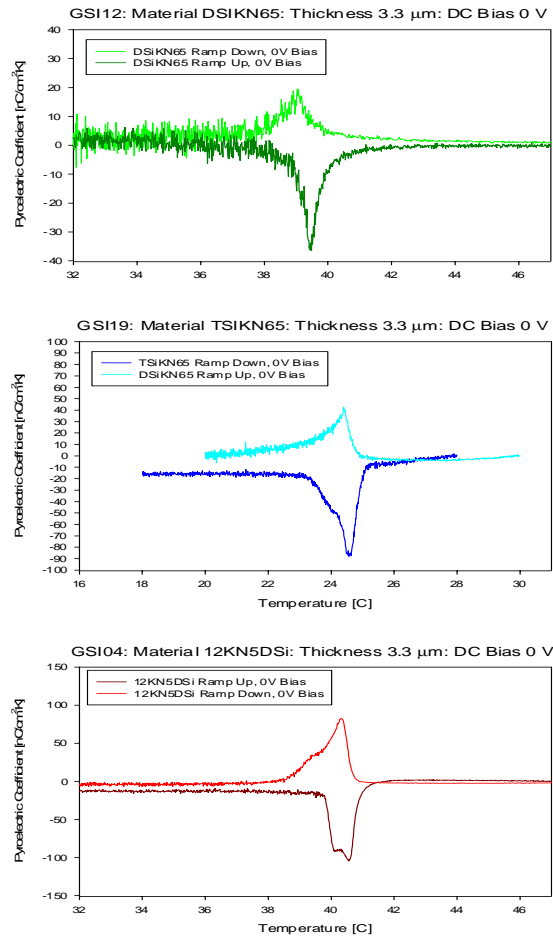


Figure 4: Pyroelectric coefficient with Zero DC bias calculated from the Byer-Roundy current data for materials a) DSiKN65, b) TSiKN65, c) 12KN5DSi.

These figures reveal several important features:

- 1) Even without any applied bias voltage, all the materials exhibit p values that are in the range 30 –100 nC/cm²K.
- 2) Such large values demonstrate the existence of strong polar order of the liquid crystal molecules.
- 3) It is also important to note that liquid crystals are essentially fluid with layer ordering only in one dimension. Considering this factor, it is remarkable that there is such a large dipolar order (as evidenced by large p values) without any bias voltage. This is due to the strong surface interaction of the aligning layer with the liquid crystal molecules.

We have also measured the pyroelectric coefficients for each sample under an applied DC bias. The application of a bias is expected to improve the dipolar order in the material, resulting in larger pyroelectric currents. However, a high bias field may also mask the pyroelectric current in a background of DC resistive current. In Figures 4 a-c we report the pyroelectric coefficient under 1V DC bias conditions. Initial attempts were made to subtract the DC component of the data and as this is non-trivial and incomplete, the data is provided with only a baseline subtraction at the high temperature end of the data. In Figure 4a, we include preliminary measurements of the DC resistance current. It is included to show that the sloped component of the pyroelectric current is quantitatively similar and therefore attributed to the changing resistance of the samples as a function of temperature. Accurate measurements of the this background current are currently underway.

Figure of Merit for uncooled IR sensor applications:

The figure of merit (FOM) for an uncooled IR sensor⁴ is determined through the following equation:

$$\text{FOM} = p / (\epsilon \cdot d \cdot \tan \delta)^{1/2},$$

where p is the pyroelectric coefficient, d is the thickness of the sensor element, ϵ is the real part of the dielectric constant and $\tan \delta$ is the dielectric loss tangent. As seen from the expression, p should be maximized while ϵ , d and $\tan \delta$ will have to be minimized. An important feature of the liquid crystalline materials is that these are “improper ferroelectrics”. This is because ferroelectricity or spontaneous polarization, is not an intrinsic property as in ferroelectric ceramics, but is derived from the molecular tilt within the layer and the symmetry breaking effects associated with the tilting. This implies that ferroelectric liquid crystals should exhibit much smaller dielectric constants than ferroelectric ceramics that are “proper ferroelectrics”. Although, ϵ and $\tan \delta$ are dependent on frequency, since an IR sensing device is normally operated at 30 Hz, we have measured the real and imaginary parts of ϵ and hence $\tan \delta$ at this frequency.

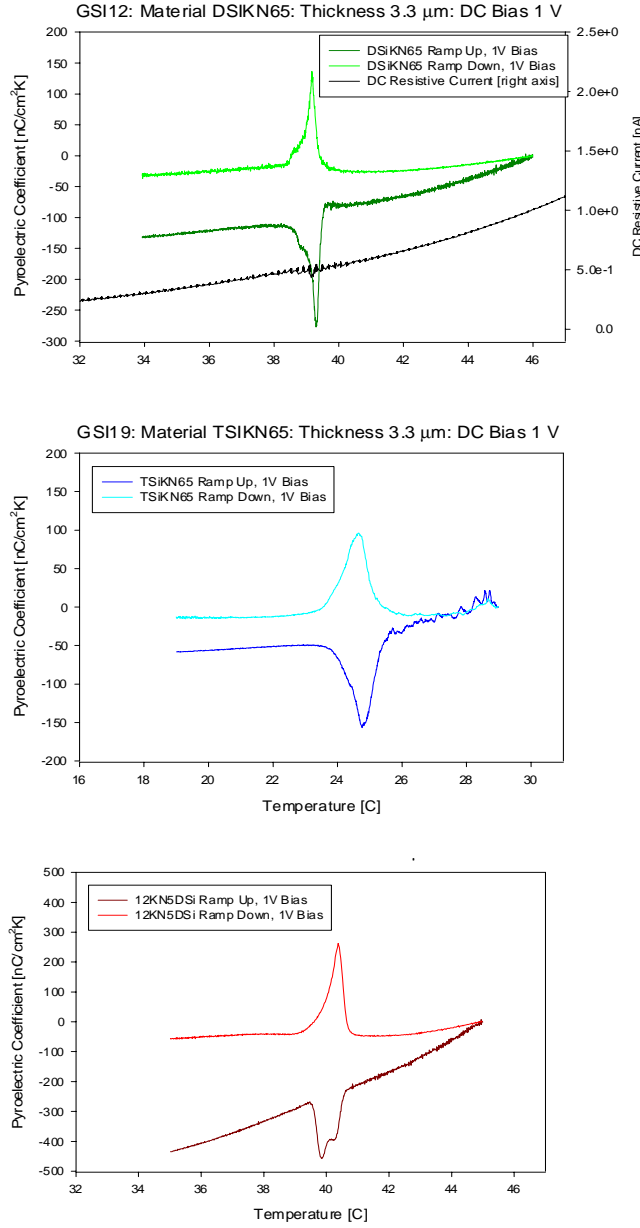


Figure 5. Pyroelectric coefficient with 1 V. DC bias applied calculated from the Byer-Roundy current data for materials a) DSiKN65, b) TSiKN65, c) 12KN5DSi. Figure 5 a. includes DC resistance data that supports our assumption that the inherent slope in the data is due to resistive current.

For a typical material like 12KN5DSi (for which we have shown the p values under zero and 1 V bias in Figs. 4c and 5c), values of ϵ and $\tan \delta$ (measured at a bias voltage of 1 volt/micron) are about 10 and 0.07 respectively. These parameters have been determined using the very same

cells that were used for the pyroelectric measurements. Compared to the ceramics that are being currently studied which have ϵ values of about 100 or more and p values of about 25, the liquid crystal materials studied here have a *much higher* p and *much lower* ϵ values. Thus, although the FOM values for our liquid crystal materials is yet to be determined accurately, the values determined so far for the pyroelectric liquid crystals appear to be promising for uncooled IR sensor applications.

4. Acknowledgements

We are thankful to Dr. Charles Hanson and Mr. Howard Beratan, Raytheon, for extremely valuable discussions. Financial support of the Office of Naval Research is gratefully acknowledged.

5. References

1. See e.g. L. M. Blinov, Mol. Cryst. Liq. Cryst. **191**, 363 (1990).
2. L. A. Beresnev, Ferroelectrics, **33**, 129 (1981).
3. C. Hanson, H. Beratan, R. Oween and G. Shelton, Proc. IRIS Passive Sensors, **1**, 29 (1993).
4. J. Naciri, et. al. (to be published).
5. C. Hanson and H. Beraton, Private Communications.